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Testing Greco-Roman medicinal minerals: The case of solfataric alum

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ABSTRACT

The medicinal minerals of antiquity reported in Greco-Latin texts are now understood to consist primarily of layered silicates, sulphates and metal oxides/sulphides, normally not in their natural state but following some processing. Recent microbiological work on layered silicates from some volcanic islands in the Aegean (Samos) and on samples of archaeological earths in museum collections (*terra sigillata*, Lemnos), has shown them to be antibacterial. This paper focuses on aluminium sulphates and in particular solfataric alum efflorescences, known to have been worked in the antiquity and later periods. The results suggest that solfataric alum consists primarily of the minerals alunogen and alum-(K) and displays strong antibacterial properties. Given that presently there is a drive to discover and develop new drugs (antibacterials) from 'extreme' environments, we suggest that an understanding of the nature and properties of sulphate-based Greco-Roman medicinal minerals in the context of the volcanic landscapes from which they derive may prove to be a worthwhile task. This paper sets the mineralogical background to some of these potentially important antibacterials, prior to delving into further microbiological work, currently underway.

1. Introduction

The medicinal properties of mineral pigments, mordants or washing powders presented in Pliny's 35th book of *Natural History* and in those of other authors of the Greco-Roman world (Galen, Dioscorides, Scribonius) have been relatively little researched compared to their botanical counterparts. Uncertainties regarding the exact nature of the minerals involved and/or the ailments they are purported to have cured have been among the contributing factors. Over the last twenty years we have carried out detailed geoarchaeological prospection and chemical/mineralogical analysis aiming to identify some of these minerals in their recorded places of origin, largely on volcanic islands in the Aegean (Hall et al., 2003a, 2003b; Photos-Jones and Hall, 2011). Furthermore, we have put forward suggestions as to how they may have been processed and assayed (Hall and Photos-Jones, 2005, 2009; Photos-Jones and Hall, 2010). In the last two years we have begun to undertake microbiological testing for the purpose of establishing whether some of these minerals are antibacterial or not (Photos-Jones et al., 2015; Photos-Jones et al., in press).

While work so far has focused on layered silicates, this paper delves into sulphur and sulphates and in particular solfataric alum-(K) (potassium-rich aluminium sulphate) efflorescences from two volcanic landscapes, in Greece and Italy: Campi Flegrei, Naples, Italy (Fig. 1a) and Melos, Western Cyclades, Greece (Fig. 2a). The reason these two areas have been chosen is because solfataric activity is relatively rare and also because both areas are known to have been exploited in antiquity and later periods (Singer, 1948; Pittinger, 1975; McNulty, 2000). Campi Flegrei (Phlegrean Fields) meaning "burning fields", is a name given by early Greek settlers (Euboeans) at Cumae, in the Bay of Naples in the 8th century BC. It is likely that these early colonists arrived there following trade routes established since the Bronze Age. Amongst the earliest dated Mycenaean sherds to be found in Italy are those from the Bay of Naples on Vivara, Procida (LH I–II: 1700–1400 BC) and on Ischia (LH IIIA: 1400–1330 BC) (Jones et al., 2014). It has been commonly assumed that the alum (*tu-ru-pte-ri-ya*) mentioned in the Linear B Knossos and Pylos tablets was aimed for the textile industry of the Mycenaean world and its allies (Firth, 2007); there has been little suggestion that it may have been medicinal as well. In the archaeological literature solfataric alum, as opposed to alum from alunite or pyritic shales, has received relatively little exposure (Borgard et al., 2005). However, recent work on Melos has highlighted archaeological evidence for the likely exploration of these efflorescences in the Roman

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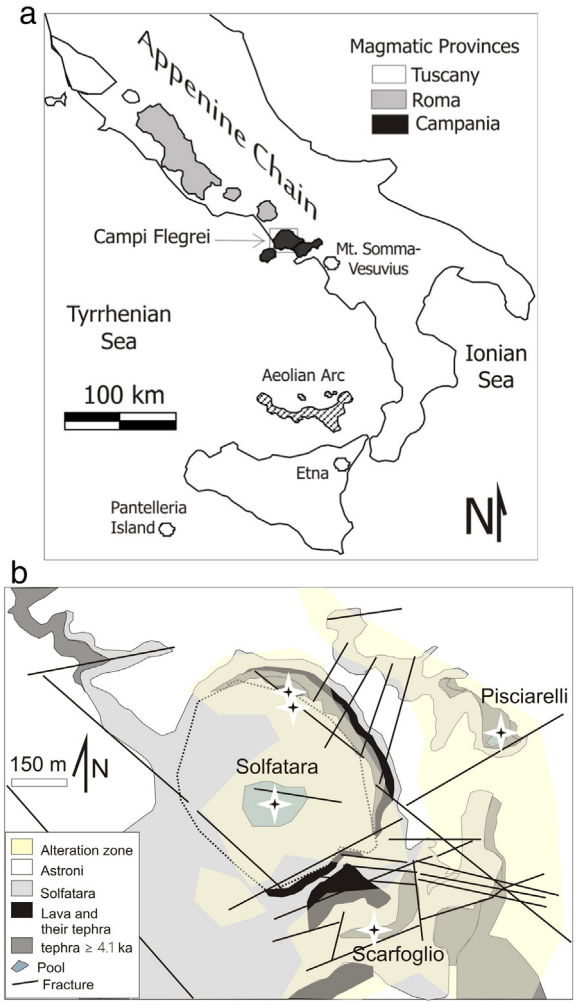

Fig. 1. a. Map of Italy with highlighted area of the Campi Flegrei, near Mt Vesuvius, Naples, Italy. b. Volcanological map of the Solfatara maar of the Campi Flegrei (adapted from Isaia et al., 2015) with sampled sites (stars). Yellow shaded field is the main alteration zone (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

period and perhaps earlier (McNulty, 2000; Photos-Jones and Hall, 2014b). We have suggested that solfataric alum was likely to have been the source of early medicinal alum (Photos-Jones and Hall, 2014a, 2014b).

Greco-Latin texts make ample reference to a number of medicinal minerals. Pliny's alum (*alumen)* referred to a) a single mineral, usually alum-(K) ($KAl(SO_4)_2 \cdot 12H_2O$) (see Table 1 for minerals mentioned in the text) and b) a group of minerals (‘*plura et eius genera*’) (Pliny, *Nat. Hist.* 35.52). From a historical and archaeological perspective, the use of alum from antiquity to recent periods has been primarily focused on the tanning and dyeing industries. Yet medicinal use is amongst the earliest documented in Egyptian medical treatises as well as Assyrian and Babylonian texts (Trease, 1964). Alum is recorded as an item of trade in the Linear B tablets of the Mycenaean period (Bennett and Olivier, 1973). Alum was extracted primarily from Melos (Cyclades, Greece), Lipari (Aeolian Islands, Italy) and Egypt (Pliny, *Nat. Hist.* 35.52). In colour it was white or greyish-white but also dark; its taste was strongly astringent, and it smelt of fire (sulphur), both sensory tests (smell and taste) being critical for its identification. As an astringent it caused the shrinkage of mucous membranes, hence its role as a hemostatic. It was used in gilding (*Nat. Hist*. 33.20) and for purifying gold (*Nat. Hist.* 35.52); as a mordant for fixing and enhancing dyes (*Nat. Hist.* 33.88); also as a flame retardant (Claudius Quadrigarius, *Annals* 19. fr.81). As a medicinal it was thought, amongst its many other external applications, to diminish offensive odours and reduce sweating (Pliny, *Nat. Hist.* 35.52). In all cases it would be the water soluble alum that was of interest, the most common one being potassium alum (alum-(K)).

Historically alum-(K) has been obtained from two main sources: first, from alunite, ($KAl_3(SO_4)_2(OH)_6$) (Table 1), via roasting in a kiln. Alum-(K) was generated and recovered by lixiviation (sprinkling or immersing the roasted mass in water to allow the alum-(K) to go into solution) and finally heating that solution to evaporation and subsequent crystallisation of alum-(K) (Singer 1948, 52). Installations for the conversion of alunite to potassium alum have been found on the island of Lesbos in the North Eastern Aegean, dating to the early Byzantine period (Archontidou et al., 2005; Archontidou, 2005). In Italy, alunite was extensively worked in the post-medieval period at Tolfa, Tuscany (Singer 1948, 139). The second historical industrial pathway for the production of Alum-(K) was via oxidation of pyritic shales to convert sulphides to sulphates; these in turn would react with the aluminium in the clay minerals of the shale, with addition of water; again pure alum-(K) would be obtained through evaporation and crystallisation (Singer 1948, 75). The archaeological evidence for the working of pyritic shales, which in Europe post-dates the 15th century, is well documented (Millard, 1999).

This paper examines the chemistry, mineralogy and microbiology of a select number of samples from the two regions. It seeks to set the alum minerals within the healing context of the Greco-Roman world, since contemporary literature makes it absolutely clear that it was (amongst other applications) medicinal as well. Volcanic landscapes in the Mediterranean have long been acknowledged for their therapeutic attributes deriving from their mineral waters (Katsambas and Antoniou, 1996; Andreassi and Flori, 1996), minerals or muds (Carretero et al., 2006; Gomes, 2013). Therefore this paper sets alum minerals within landscapes long considered therapeutic but with a renewed agenda. This agenda, part of a longer term project, the pilot stage of which has just started (*), will follow a methodology aimed at establishing the relationship between minerals and the microbiome they co-habit; this means the micro-organisms (bacteria, algae, fungi) in the vicinity of which they are often found and asks the question: are these microorganisms responsible for attributing medicinal (antibacterial/antifungal) properties to the minerals on which they grow? We argue that this holistic approach, whereupon minerals are examined as part of, rather than the sole occupants of a particular habitat, closely approximates the approach that would have been followed by the doctors and healers of antiquity. Their medical prescriptions were largely based on sensory evaluation and empirical understanding of the landscape from which they drew their raw materials, mineral or botanical. This paper helps to set the scene for this holistic approach by focusing primarily on the mineralogy of solfataric alum; also by demonstrating the antibacterial properties of a small number of samples thereof.

1.1. Solfataric landscapes: Campi Flegrei and Melos

Campi Flegrei are located in the Neapolitan area, between Agnano and Pozzuoli and include the three sampling localities of Solfatara, Pisciarelli and Scarfoglio (Fig. 1a and b). This territory is a quaternary volcanic field characterised by a thermal gradient reaching up to 150 °C/km (Piochi et al., 2014). Degassing produces predominantly water and to a lesser extent CO_2 and H_2S. The volcanic rocks are typically K-rich and generally with low content of alkali feldspar phenocrysts.

The crater of Solfatara (Figs. 1b and 3a), and its east and south slopes at Pisciarelli (Figs. 1b and 3b) and Scarfoglio (Fig. 1b), are part of the homonymous maar generated since 4200 ky BP and characterised by pyroclastic deposits and lava flows/domes (Isaia et al., 2015). The maar hosts an acid sulfate alteration environment developed on trachyte pyroclastic deposits and lavas (Valentino et al., 1999; Valentino and Stanzione, 2004; Glamoclija et al., 2004; Piochi et al., 2015; Mayer et al., 2016). Solfatara is the type locality of alum-(K) (Ciriotti et al.,

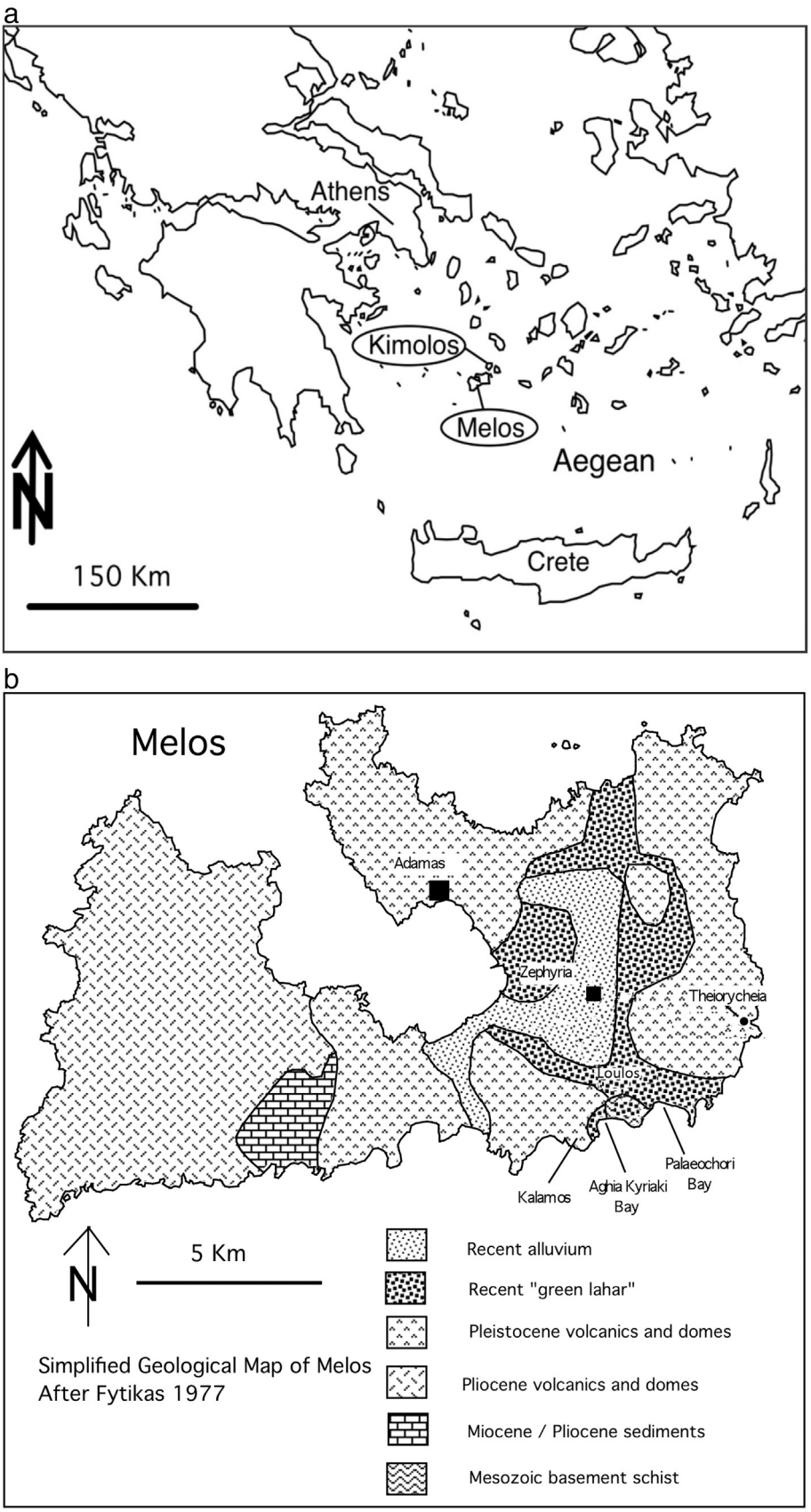

Fig. 2. a. Map of Greece showing the islands of Melos and Kimolos in the western Cyclades, Greece. b. Map of Melos showing the localities of Loulos, Kalamos and Fyriplaka crater on the northern edge of the Kalamos peninsula (adapted from Photos-Jones and Hall, 2014b).

Table 1
List of ideal crystal-chemical formulas of minerals quoted in the text and associated with Melian and Campi Flegrei solfataric alum.

Minerals	Ideal formulas*
Alum-(K)	$KAl(SO_4)_2 \cdot 12(H_2O)$
Alunite	$KAl_3(SO_4)_2(OH)_6$
Alunogen	$Al_2(SO_4)_3 \cdot 17H_2O$
Analbite	$NaAlSi_3O_8$
Analcime	$Na_2(Al_2Si_4O_{12}) \cdot 2H_2O$
Anatase	TiO_2
Anhydrite	$CaSO_4$
Anorthoclase	$(Na,K)AlSi_3O_8$
Cinnabar	HgS
Clinoptilolite	$(Na,K,Ca)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36} \cdot 12(H_2O)$
Cristobalite	SiO_2
Diopside	$CaMgSi_2O_6$
Dolomite	$CaMg(CO_3)_2$
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26(H_2O)$
Gypsum	$CaSO_4 \cdot 2H_2O$
Hematite	Fe_2O_3
Hydrobasaluminite	$Al_4(SO_4)(OH)_{10} \cdot 12\text{-}36(H_2O)$
Kaolinite	$Al_2Si_2O_5(OH)_2$
Millosevichite	$Al_2(SO_4)_3$
Montmorillonite	$(Na,Ca)_{0.3}(Al_{1.7},Mg_{0.3})_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$
Muscovite	$KAl_2(AlSi_3O_{10})(OH,F)_2$
Pyrite	FeS_2
Quartz	SiO_2
Sanidine (K-feldspar)	$KAlSi_3O_8$
Steklite	$KAl(SO_4)_2$
Sulphur	S
Tschermigite	$(NH_4)Al(SO_4)_2 \cdot 12H_2O$

* From webmineral.com.

2009); the mineral occurs as fumarolic or solfataric precipitate genetically linked to the oxidised form of sulphur vapour. Its action on the K-rich Al-bearing silicate rocks, which are likely to contain altered pyrite, is roughly similarly to Melos. Alum is detected among the secondary mineralogical assemblage, particularly in the mudpools (Fig. 3b).

Pozzuoli was well known for its 'aluminous baths', the sweating or sudatory baths mentioned first by Livy, and later in the 7th C by Isidore of Seville and the Salerno school doctors in the 12th century (Singer, 1943, 1948). One was located at Pisciarelli (Fig. 1b), and was called the *Bulla*, the bubbling one; it disappeared after the eruption of the 27th of September 1538 which gave rise to the Mount Nuovo volcano, west of Pozzuoli (Di Vito et al., 1987). In the early 17th century, alum-producing activities focused alternatively either within the crater of the solfatara or to the NE and E. In 1604 it was reported that there were 2000 fumaroli exhaling sulphurous, aluminous and ammonia vapours, some of which were medicinal (Capacio (1604) in Singer 1948, 168). A few years later, in 1610, eyewitness accounts reported that the minerals of alum to the east of the Solfatara were the best in the world (Sandy (1610) in Singer 1948, 169). A guide book by Pompeo Sarnelli dated 1692 reported that '*rain water carrying in solution the aluminous substance of the solfatara, was collected in tanks, while alum stone from within the crater continued to be treated at the old works outside the crater*' (Sarnelli (1692) in Singer 1948, 171) suggesting exploitation of both alunite and efflorescences, in parallel. The same guide book reports that earlier in 1687 an industrialist from Bergamo refined alum on the spot: '*the rainwater* (full of the aluminous substance) *drained from the plain, they boil most marvellously in three large buried leaden cauldrons wherein the lye is cleared*'. The buried pots suggest the use of the local geothermal field.

Sir William Hamilton visiting the area in the 18th century confirmed the continuation of that practice: '*by mixing earth of this plain (solfatara) with water of the Pisciarelli in leaden cauldrons heated merely by volcanic fire of the spot on which they are placed alum is produced*' (Hamilton (1776) in Singer 1948, 203). Hamilton also notes the presence of crystals of '*beautiful red colour*' (he calls it cinnabar) and the extraction of salammoniac: '*Near Astruni, and towards the sea rises the Solfatara which not only retains its crater and cone but also its former heat. In the plain smoke issues from many parts as also from its sides. Here by means of stones and tiles heaped over the crevices, through which the smoke passes, they collect in an awkward manner what they call sale armoniaco*' (Hamilton (1776) in Singer 1948, 174). However, it is mainly Fougeroux de Bondaroy (1768) (in Singer 1948, 172)), a mining expert who visited Pozzuoli who gave the most detailed account of the extraction and processing of the alum-(K) efflorescences as well as a plan of the installations. Fougeroux's plan of the interior of a hut where alum was processed (Fig. 5) is reproduced here from Singer (1948, Fig. 103); the layout of the central tank and adjacent cauldrons throws light on what must have been established practice, i.e. the processing of raw alum via a cycle of dissolution-evaporation. Fougeroux's description makes clear that the hot soils of the Solfatara were used as an energy source for the dissolution of alum-rich earths within the long tank in the centre of the hut. The supernatant alum-rich liquid would then be transferred, from the tank into the adjacent cauldrons, where it was allowed to slowly evaporate to near dryness. It is understood that the insoluble material in the tank would be discarded.

Melos (Fig. 2a,b) is dominated by Tertiary and Quaternary hydrothermally altered felsic volcanic rocks (Fytikas, 1977; Shelford, 1982). The metamorphic basement is only partially exposed. Melos has some present-day minor geothermal activity both on-shore and off-shore with the high geothermal gradient focused on Zephyria (Fytikas, 1989; Botz et al., 1996). Alum-rich sulphurous fumaroles in Melos occur not only in open air but also underground in cavities in the area of Kalamos (Figs. 2b and 4a), a promontory in the SE of the island consisting of volcanic tuffs and volcanoclastic domes. Many of these cavities were opened at unspecified time for the purpose of accessing these minerals. They are now revealed as a result of open cast mining. A model for the origin of aluminium-rich efflorescences near fumaroles has been presented by Hall et al. (2003a). The sulphur of these emissions is oxidised to sulphuric acid under the action of rain water. Under its action metals like aluminium are leached out of the original Al-silicate minerals (K-feldspars, micas) and the volcanic glass present in the volcanic rocks. Al-sulphates, mostly alunogen, form and are precipitated, upon cooling, at the fumarole entry. They are very soluble and will readily dissolve unless in a cavity recess. While aluminium sulphates are efflorescences, sulphur is the product of desublimation from S-rich (solfatara) vapours. Kalamos (Figs. 2b and 4a), Loulos and Fyriplaka cavern, in the immediate vicinity of Kalamos, are likely candidate localities for the extraction of alum in the Roman and most likely other periods, as well.

In antiquity Melian alum was traded under two commercial names: *phorimon* and *paraphoron* (Pliny, *Nat. Hist.* 35.52). The former was liquid, the latter was solid. Solid alum consisted of different varieties (*strongyle* (round), *trichitis or schiston* (feathery alum)). Dioscorides (*De Materia Medica* 5.123) suggested that *for medicinal use, both ye Scissilis (schiston), and the Round (strongyle), and ye Moist is taken; but ye Scissilis is the best*" (Gunther 1934, 643). 'Liquid' has been translated here as 'moist'. The liquid variety was the most abundant and although the translation of Pliny's *liquidum spissumque* has been much debated it now seems clear that natural liquid alum could indeed have existed (Hall and Photos-Jones, 2005, 2009; Photos-Jones and Hall, 2010). This would have occurred as a supersaturated solution of aluminium sulphate minerals, particularly alunogen, the result of degassing in an area of geothermal activity (Hall et al., 2003a,b). There are no such seepages to be seen today, suggesting that Melos's geothermal field is waning but they were observed as recently as the 18th century. Archaeological evidence for the extraction and processing of fumarolic alum in Melos in the Roman period has only recently begun to emerge. Although there is as yet no clear evidence for a workshop, there are a number of localities, for example, Aghia Kyriaki on the bay at the foothills of Kalamos, with abundant industrial pottery consisting of shallow open vessels, but also large quantities of large storage jars and transport

Fig. 3. a. View of the Campi Flegrei Solfatara crater with a single grinding millstone in the foreground for the grinding of the 'bianchetto', purported to be extracted in the Roman period. It is not clear what the exact nature of the 'bianchetto' was. In the background (to the right) is the mud pool which was relatively dry at the time of the visit (July 2015). This mud pool was the source of sample 720.35. b. View of the Pisciarelli with mudpool (stream) on the foreground, the source of sample 720.50.

amphorae (Photos-Jones et al., 1999; McNulty, 2000; Photos-Jones and Hall, 2014b; Le Quéré, 2015).

2. Materials and methods

2.1. Sampling

Thirty samples (Table 2a and b) were collected from three localities within Campi Flegrei (Pisciarelli, Solfatara and Scarfoglio) and three localities in the greater Kalamos area, SE Melos, to include the Kalamos tunnels, Fyriplaka cavern and Loulos quarry. Sampling focused primarily on efflorescences and the underlying host rock, in varying proportions. At Campi Flegrei sampling focused on: (i) the Solfatara's whitish altered pyroclastic deposits in the vicinity of the old restored *stuffe* (brick structures built around the steam vents and acting like saunas) and a slightly altered lava inside the crater; (ii) the Solfatara's, mostly dried-up, mudpool and the Pisciarelli 'boiling' mudpool; (iii); encrustations forming around the main degassing vents; (iv) deposits from the vertical walls of the Pisciarelli and Scarfoglio scarps. The Melos samples targeted occurrences of alum-(K) evidenced as fluffy, whitish crystals (Fig. 4b) but also hard rock of white or pale red colouration from a) within the Kalamos galleries and from around vents, b) the Fyriplaka cavern and c) the Loulos abandoned quarry, near the locality of the newly formed degassing vent; also sulphur (Fig. 4c). Both Kalamos and Loulos were quarried for kaolin from the 1950s to the 1970s; given the scale of these activities, it is likely that any sign of earlier activities (i.e. in antiquity) is probably now largely obliterated.

2.2. Mineralogy

The mineralogical composition of the samples from both study areas was determined with X-ray diffraction (XRD). Those from the Campi Flegrei were examined at the Istituto Nazionale di Geofisica e Vulcanologia—Osservatorio Vesuviano (Napoli) with an X'Pert Powder

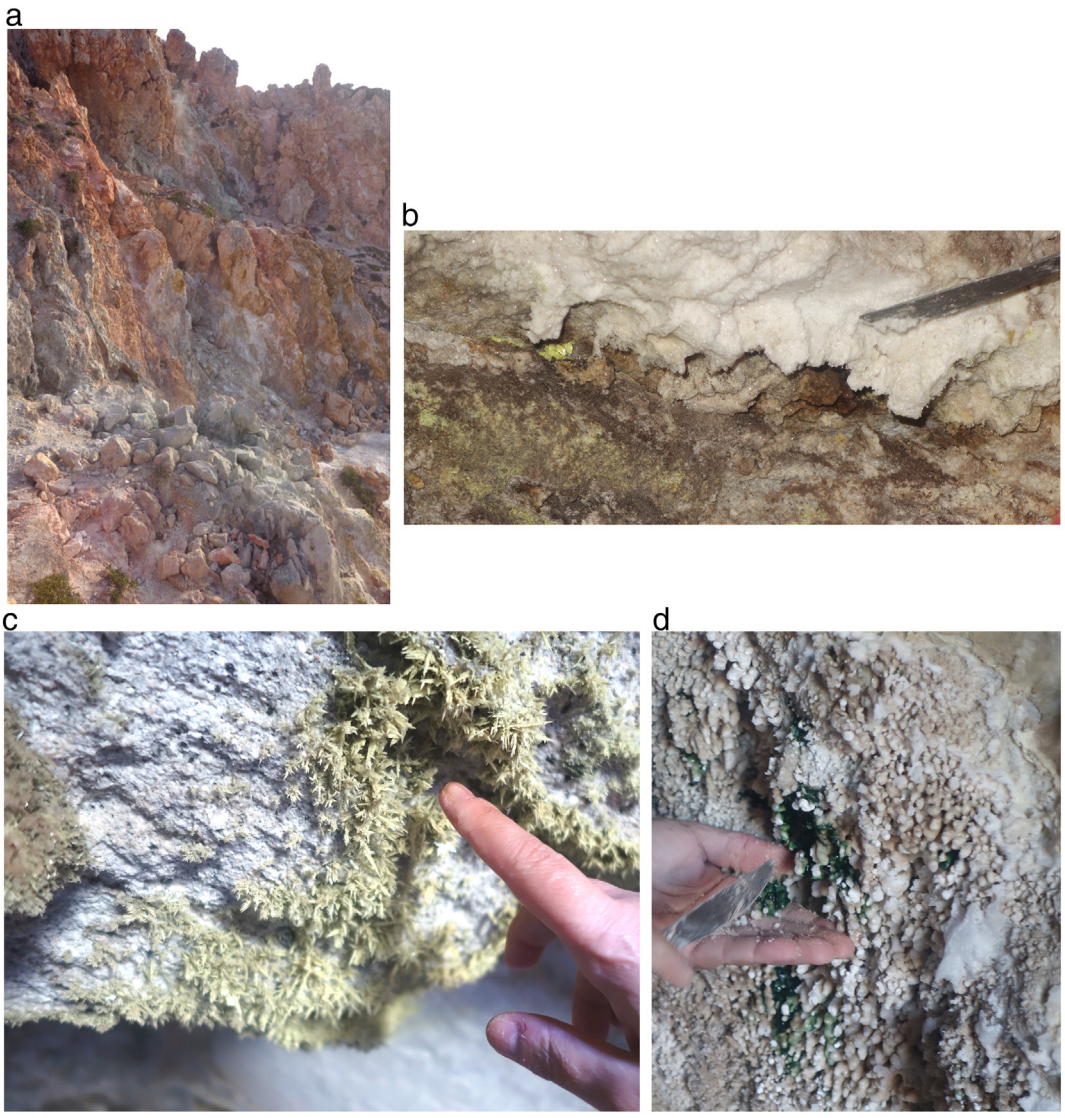

Fig. 4. a. Active fumaroles seen in Kalamos, SE Melos. b. Thick layer of fresh alunogen-rich efflorescences which can be easily removed from the cavern wall, Fyriplaka cavern, Fyriplaka crater, SE Melos. c.Yellow sulphur crystals forming as a result of desublimation around vents, Kalamos. d. Microbial growth (green patch) amidst moist alunogen-rich efflorescences and other, possibly silicified, mineralisation. The microbial ecology of Kalamos is currently under investigation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

diffractometer (PANalytical) equipped with a high speed PIXcel detector, using Ni-filtered, CuKα radiation, pyrolytic graphite crystal monochromator, 40 kV and 40 mA in a 3–70°2θ range, a step size of 0.02° and scanning time 8 s/step. The samples were air-dried for one week and then sealed. Part of them was in water and soluble portion was dried to produce an alum enriched fraction. Prior to XRD analysis the bulk and enriched fractions were examined with a binocular microscopy. The diffraction patterns were interpreted by using the X'Pert HIGH Score Plus computer program and JCPDS PDF-2 database. For quantitative analysis of X-ray diffraction patterns, the samples were mixed with 10% in weight of the reference corundum standard material (NIST SRM 674a) and were refined with HighScore Plus software with Rietveld structural models based on the American Mineralogical Crystal Structure Database (AMCSD). The results are presented in Table 2a.

Samples collected from Melos were examined at the School of Mineral Resources Engineering, Technical University of Crete, on a Bruker D8 Advance Diffractometer equipped with a Lynx Eye strip silicon detector, using Ni-filtered CuKα radiation (35 kV, 35 mA). Data were collected in the 2θ range 3–70° 2θ with a step size of 0.02° and counting time 1 s per strip step (total time 63.6 s per step). The XRD traces were analyzed and interpreted with the Diffrac Plus software package from Bruker and the Powder Diffraction File (PDF). The quantitative analysis was performed on random powder samples (side loading mounting) by the Rietveld method using the Autoquan© software package version 2.8. The results are presented in Table 2b.

2.3. Geochemistry

The chemical composition of the samples was determined with ICP-MS (7500CX coupled with Autosampler Series 3000, both by Agilent Technologies), at the University of Crete. About 200 mg of each sample was digested with 8 mL aqua regia in a microwave digestion device (Multiwave 3000, Anton Paar), following the EPA3051 method (Anton Paar digestion protocol). The method is not suitable for determination of Si and major elements in general due to partial dissolution of the silicates and neither of S, due to analytical constraints. The precision of the analyses was tested using suitable standards. The relative standard

deviation of the analyses varied according to the concentration, typically 7% for the major elements, less for the trace elements.

2.4. Experimental minerals processing

In this section we investigate the effect of heating of the raw minerals, under field conditions, and for the purposes of establishing possible changes in the composition of the raw solfataric alum. Similar field-based experiments have been carried out previously using the hot soils of a solfatara in Melos (Hall and Photos-Jones, 2005). In this case two samples were chosen, (720.9 and 720.14b, Table 2b) both from Kalamos. *c.* 70 g of the sample was added to 500 ml of tap water in a plastic bottle and the suspension was shaken and allowed to settle overnight. Subsequently, in sample 720.9, the clear supernatant liquid was decanted in an (aluminium) pan and was heated to dryness at ~180 °C on a hot plate (dry sample 720.9.1). The remaining material, which consisted of a thick milky colloidal suspension and an undissolved fraction, passed through a cloth sieve. Both, the solid material retained by the cloth sieve (sub-sample 720.9.3), and the alum-rich solution passing through the sieve (sub-sample 720.9.2) were collected. 720.9.2 was subsequently heated on a hot plate to dryness and the solid residue collected and analysed. 720.9.3 was also analysed. In the case of sample 720.14b, two subsamples were collected: the undissolved material (sub-sample 720.14b.3) retained by the cloth sieve and the supernatant liquid over the undissolved material (sub-sample 720.14b.1). The latter had been heated on a hot plate and the residue was collected. All subsamples were analysed by XRD and ICP (see Tables 2c and 3).

2.5. Microbiology

Two samples, 700.11(527) and 700.14(659) (Table 2b), were prepared for microbiological testing by grinding into fine powders and subsequent sterilisation by dry heat at 200 °C for 2 h. Three micro-organisms, a Gram positive bacterium (*Staphylococcus aureus* ATCC 25923), a Gram negative bacterium (*Pseudomonas aeruginosa* ATCC 27853), and a yeast (*Candida parapsilosis* ATCC 22019) were chosen for testing. A 0.5 McFarland dilution (a standard dilution of micro-organisms utilising optical density to create a standard inoculum) of each organism was made using sterile saline and a densitometer. 400 μl of this microbial suspension was added to a sterile micro tube containing 200 mg of sample. Note that *Candida parapsilosis* was only tested against 700.14(659), whereas each bacterial strain (*Staphylococcus aureus* and *Pseudomonas aeruginosa*) was tested against both 700.11(527) and 700.14(659). Positive and negative controls were included, consisting of (a) microbial suspension only (with no sample added) and (b) sample only (400 μl of sterile saline added instead of microbial suspension). Each combination was set up in triplicate. The micro tubes were then incubated overnight in an upright position at 37 °C, on top of a rotating mixer to help prevent sedimentation. To estimate microbial counts, 10-fold serial dilutions were made using sterile saline and (a) the microbial suspensions prior to overnight incubation, (b) the microbial suspensions following overnight incubation, and (c) the microbial suspensions + sample following overnight incubation. 10 μl of each dilution was plated onto blood agar in duplicate and incubated overnight at 37 °C. Following overnight incubation of these plates, microbial counts were quantified by counting the number of colony forming units on each plate. Results are displayed as a combined graph in Fig. 7.

3. Results

3.1. Mineralogy of the geological samples

The results of the quantitative analyses of the Campi Flegrei (CF) and Melos samples are shown in Table 2a and b. The alteration mineral assemblage is mainly composed of a mixture of alunogen, alum-(K), alunite, native sulphur and rare gypsum (Fig. 4b and c); there is also a large proportion of amorphous material. Alunogen is dominant in the Melos samples 720.1, 5, 6, 13, 18 with alum-K not exceeding *c.*10%. Alum-(K) is more common in the CF samples; hematite can reach on a localised scale up to *c.* 24% (Pisciarelli sample 720.51, Table 2a). In the Melos samples alunite is evident but not in association with alunogen (with the exception of 720.14b) but rather with kaolinite and quartz. In the CF samples, alunite is the dominant phase, sometimes associated with alunogen; Alum-(K) may not be present while hematite excludes the occurrence of Alum-(K).

The association of alunite with kaolinite in the Melos samples is typical of advanced argillic alteration occurring at low pH indicating extensive leaching conditions. In any case the development of argillic alteration should not be linked to the formation of alunogen, alum-(K) and hydrobasaluminite. Indeed, kaolin deposits in which kaolinite may be associated with alunite and jarosite but not with alunogen are widespread in the Mediterranean and South America (Bristow, 1987; Dill et al., 1997; Ece and Schroeder, 2007). On Melos, apart from the areas of Loulos and Kalamos, alunite-bearing kaolins occur around Ralaki and Kastriani (Christidis and Marcopoulos, 1995) in the NW and SE of the island respectively. Alunite and jarosite do not form as desublimates from acidic vapours and so their association with alunogen and alum-(K) probably represents different hydrothermal episodes.

An additional difference between the two areas is the presence of abundant amorphous matter in Campi Flegrei samples. It has been suggested (Piochi et al., 2015; Mayer et al., 2016) that the amorphous fraction can represent both the primary volcanic glass material and/or alteration products, i.e., the amorphous SiO_2 (opal-A) precipitated by prolonged acid hydrothermalism. The Kalamos samples contain abundant SiO_2-polymorphs (quartz and cristobalite) which are compatible with the Si-saturated precursor rocks present in the area (Fytikas, 1977). However, the modern hydrothermal solutions in the Paleochori-Aghia Kyriaki area, in the vicinity of Kalamos, (Fig. 2b), are rich in Si (Valsami-Jones et al., 2005). This suggests that at least part of these SiO_2-polymorphs might be due to recrystallization of amorphous SiO_2 precipitated from these solutions. Although no attempt was made to determine the amount of amorphous matter in the Kalamos samples (Table 2b) (lack of adequate amount of sample did not allow the use of internal standard for determination of amorphous matter), its content is not considered important owing to the lack of a significant hump in the 2θ range 18–30°; an amorphous content of at least 15–20% would be necessary to create such a hump in the diffractogram.

At Kalamos, solfatara activity yielded also hydrobasaluminite, whereas in the Campi Flegrei samples traces of tschermigite (ammonium-bearing alum, see Tables 1 and 2a) were detected. In addition, the Campi Flegrei samples contain traces of pyrite and cinnabar, while the Kalamos samples contain also feldspars (both plagioclase and K-feldspar) and anatase and in one sample (720.2) smectite and clinoptilolite (Table 2a and b). In the Campi Flegrei samples there are sanidine, diopside, hematite, muscovite/illite, montmorillonite and analcime (Table 2a). Cinnabar mineralization is likely to derive from native mercury which is closely associated with hot springs (Siegel et al., 1973). Otherwise, the ammonium occurrence could be due to microbial metabolic activity such as nitrification processes. The presence of ammonia could show a biogenic component for the formation of tschermigite that also merits further investigation. In any case, salammoniac occurs as a sublimate phase at Solfatara in the high temperature fumaroles (T > 100 °C) associated with realgar and sulphur (Russo, 2004). Reference to the extraction and processing of both ammonium and other minerals is clearly made by Sir William Hamilton (see reference to salammoniac in section on History above) but in the areas we selected ammonium sulphates were not present.

3.2. Chemistry of the geological samples

The results of ICP-MS trace element analysis are listed in Table 3. Although it would have been important to be able to fingerprint alum

Table 2
Mineral abundances from X-ray diffraction quantitative analysis of (2a) Campi Flegrei samples; note: *area* indicates different zone of sampling (2b) Melos samples (geological and processed). Data recalculated to 100%. See Table 1 for mineral formulae.

a

Location	*Sample ID*	*Sample details*	*Alunogen*	*Alunite*	*Alum-(K)*	*Hematite*	*Sanidine*	*Sulphur*	*Gypsum*
Pisciarelli	720.34	Area 1 on fumarole wall (same site L1 of Piochi et al., 2015)	40.7	7.5	12.4				
Pisciarelli	720.35	Mudpool		9.2			7.1	12.6	
Pisciarelli	720.36	Area 2 on fumarole wall (same site L1 of Piochi et al., 2015)	20.6	7.7	18.7			26.1	
Pisciarelli	720.37	Blackish encrustation on fumarole wall (same site L1 of Piochi et al., 2015)		14.0				51.8	
Pisciarelli	720.38	Greenish encrustation on fumarole wall (same site L1 of Piochi et al., 2015)	18.1	10.9	13.0				
Solfatara	720.40	Efflorescences above the brick 'stuffe'/stoves	21.5	5.2	10.8			1.4	
Pisciarelli	720.50	Mudpool (from Piochi et al., 2015, Table 2)	27.4	10.8			12.0	32.1	
Pisciarelli	720.51	same sample Red 1_1/15 in Piochi et al., 2015)		16.4		23.7			
Pisciarelli	720.52	Red alteration in site L1 of Piochi et al. (2015)		50.7		0.8			
Pisciarelli	720.53	N wall to the mud pool		26.7					
Solfatara	720.54	Cryptodome		6.3			17.5		
Scarfoglio	720.55	Dense lithic at the Igloo, E Solfatara		8.5					6.9
Scarfoglio	720.55.1	White portion at the Igloo, E Solfatara	5.2	94.8					
Scarfoglio	720.55.2	Reddish portion at the Igloo, E Solfatara					32.4		0.5

b

Location	*Sample no.*	*Description*	*Alunogen*	*Alunite*	*Alum-(K)*	*Sulphur*	*Steklite*	*Ettringite*	*Gypsum*	*Anhydrite*
Fyriplaka cavern	720.1	Alum efflorescences	91.9		2.5	5.6				
Loulos	720.2	White 'rock'		15.9						
Kalamos	720.3	White 'rock'							5.4	
Kalamos	720.5	Alum efflorescences V	99			1				
Kalamos	720.6	Alum efflorescences IV	86.4		7.9				1.9	
Kalamos	720.7	Alum efflorescences VI with organic material	30.6			69.4				
Kalamos	720.8	Alum efflorescences IV	15.2	25.3		25.1				0.7
Kalamos	720.9	Alum efflorescences VII	2.8	5.6		29.4				
Kalamos processed	720.9.2	colloidal suspension of 720.9 after heating on hotplate		12.3					5.6	
Kalamos processed	720.9.3	solid undissolved fraction of 720.9 after drying in air		8.2		28.5				
Kalamos	720.13	Alum efflorescences VIII	88.1		11.2					
Kalamos	720.14b	Alum efflorescences with white 'rock'	18.3	9.6						
Kalamos processed	720.14b.1	Soluble salts after evaporation	67.7							
Kalamos processed	720.14b.3	solid undissolved fraction of 720.14b after drying in air	4	31.4						
Kalamos	720.18	Alum efflorescences IX	98.6			1.4				
Loulos	720.30.2	White 'rock'		24.8						
Fyriplaka cavern	700.11(527)	Alum efflorescences	81.9					6.07		
Fyriplaka cavern	700.14(659)	Alum efflorescences	25.1		15.1		51.3		8.5	

efflorescences from one source or another, Italy or Greece, no particular trace element stands out. In Melos the concentration of most elements is below the limit of detection. Nevertheless, there is a marked increase in Ti, V, Sr and Pb in the CF samples, while the Melos samples are more abundant in Cr; the former present geochemical compatibility with water geochemistry (Valentino and Stanzione, 2004; Valentino et al., 1999). Although the source of Cr on Melos could be invoked in the solfatara springs, the modern hydrothermal solutions in the vicinity of Kalamos are very poor in Cr, Ni, V and Pb but they contain abundant Mn (Valsami-Jones et al., 2005). The higher Ti and V contents appear associated to Ti oxides, while the presence of Mn of the Melos samples might be related to Mn oxides precipitated from the hydrothermal solutions. Sr and Pb are directly correlated with the amorphous fraction of the CF samples, i.e. they could be leaching from and/or represent the parental rocks; however, Pb may have an endogenous or anthropogenic origin. TiO_2 minerals (anatase) are associated with the Melos samples (e.g. 720.2, 720.30.2) and might explain the titanium content in these samples.

Regarding boron content, it is very low (max. 6 ppm only in two CF samples) and in general below the detection limit for both CF samples and Melos samples (Table 3). In the case of Melos, all samples contain boron in accordance with the seawater contribution in the hydrothermal system of the island (Valsami-Jones et al., 2005; Wu et al., 2012), but there is no clear trend between the concentration of this element and the mineralogical composition. Samples 720.1 and 720.3 with the higher boron concentrations have contrasting mineralogical composition, with the former consisting of solfatara sublimates indicating very low pH, and the latter containing smectite and feldspars indicative of more alkaline conditions. The observed intense leaching is in accordance with the very low pH of the solfatara-type alteration. An in-depth assessment of trace element variation between the two data sets, part of a broader study on the provenance of alum efflorescences, is presently outwith the scope of this paper.

3.3. Mineralogy of the processed samples

The processed samples from Kalamos (samples 720.14b.1 and 720.14b.3, Table 2b) contain a rare Al-sulphate, millosevichite, which is absent from the original samples. Millosevichite is a rare anhydrous Al-sulphate which forms in volcanic areas with solfatara activity as sublimate like the present study (Hall et al., 2003a; Zelenski and Bortnikova, 2005) or in the oxidation zones of metallic ores like porphyry copper ores (Voudouris, 2011) and as secondary phase in burning coal mines (Kruszewski, 2013). Actually the type locality for millosevichite is Vulcano Island in Italy (Panichi, 1913; Ciriotti et al., 2009). In general, the formation of natural anhydrous Al-rich and Fe-rich sulphates instead of their hydrous counterparts (e.g. alunogen) indicates higher temperature formation via desublimation (Miura et al., 1994). The lack of millosevichite from the efflorescences and the presence of alunogen in Melos (as well as in CF) suggests that the sublimation temperatures might not have been high enough, probably lower than 150 °C.

In contrast, during processing, dissolution of alunogen released Al^{3+} and SO_4^{2+} in water, which precipitated as Al-sulphate when the solution was brought to total dryness at ~180 °C (Table 1). Still, even in these samples alunogen was the dominant Al-sulphate, suggesting that the

Pyrite	*Cinnabar*	*Tschermigite*	*Analcime*	*Muscovite*	*Diopside*	*Quartz*	*Montmorillonite*	*Amorphous*
								39.4
		0.4						70.7
								26.9
0.2						0.1		33.8
								57.9
								61.1
								17.7
								59.9
	0.2							48.3
0.7								72.5
								76.3
							0.2	84.4
			1.8	3.0	19.0			43.4

Anatase	*Kaolinite*	*Quartz*	*Cristobalite*	*Montmorillonite*	*Anorthoclase*	*Hydro/basaluminite*	*Dolomite*	*Muscovite*	*Clinoptilolite*	*K-feldspar*	*Plagioclase Analbite*	*Millosevichite*
0.9	80.6	0.5	2.1									
	38.8	10.1		5.3	10.5			19.3	6.9	3.7		
		3.3				0.5						
		32.8					0.9					
	2.4	59.8										
	9.3	69.7	2.1			1						1
	3.1	59.7				0.5						0.5
						0.7						
	35.5	32.7	2.7							1.2		
											32.3	
	30.2	28.8	3.4							2.2		
0.9	56.6	13.3	4.4									
			9.9								2.1	

temperature in the hot plate was not adequate to dehydrate the Al-sulphate and form millosevichite. However, the full width at half maximum of alunogen is considerably larger in the processed sample 720.14b.1 compared to the original 720.14b (Fig. 6), suggesting that alunogen also precipitated from the acidic solution during processing due to evaporation. It is considered that during processing millosevichite formed at those sections of the metal tray which hosted the Al-rich solution in which the temperature might have been higher. With the existing data it is not certain if prolonged drying might lead to conversion of alunogen to millosevichite. It is also not certain whether millosevichite has antibacterial properties; however the fact that the dissolution products of millosevichite are identical to those of alunogen strongly suggests that it should also have antibacterial properties.

An equally interesting case is to be made for steklite ($KAl(SO_4)_2$) also an anhydrous potassium alum salt. Alum salts are sensitive to local fluctuations in temperature, composition of the solfatara steam and relative humidity; this might explain why steklite is present in one sample from Fyriplaka cavern but not others.

3.4. Microbiological results

Samples, 700.11(527) and 700.14(659) (Table 2b) were tested for bioactivity against two different bacterial strains, *Staphylococcus aureus* and *Pseudomonas aeruginosa*. Sample 700.14-659 was additionally tested for bioactivity against the yeast *Candida parapsilosis*. The results are shown in Fig. 7, where the above mentioned samples are simply referred as 527 and 659. A logarithmic scale on the y axis of the graph displays the microbial counts, expressed as the mean number of colony forming units per 10 μl. The graphs illustrate the changes in microbial counts, both after an overnight's (18 h) incubation and with or without addition of samples. Error bars demonstrate the standard error of the mean (SEM), calculated on Microsoft Excel by first working out the Standard Deviation of sample results and then dividing this number by the square root of the number of samples. Significance (p value) is relative to the positive control (bacterial suspension only, i.e. no sample added, at 18 h), and was determined on Microsoft Excel using a two-tailed t-test. Only p values $<$ or $=$ 0.05 were deemed significant.

Both samples demonstrated a statistically highly significant bactericidal effect against *S. aureus* ($p = 0.04$) and *P. aeruginosa* ($p = 0.05$), reducing bacterial counts to zero following overnight (18 h) incubation. A very slight reduction in microbial counts of *C. parapsilosis* was associated with addition of 659, but this was a reduction of less than 1 log and did not reach statistical significance ($p = 0.08$).

4. Discussion

This paper has focused on the mineralogy and chemistry of solfataric alum efflorescences at Campi Flegrei, Italy and in Melos, Greece. These two areas are known to have been worked for their alum deposits during two different historical periods, i.e. in the Roman period and the 17th–18th centuries. This paper raises the following points:

The first concerns mineral composition. In both areas the solfataric alum is represented by a mixture of two main soluble minerals, alunogen and alum-(K), as well as sulphur, alunite and a host of other minerals in various concentrations. There is a plethora of minerals which could, in principle, fingerprint each region, for example ammonium salts (i.e.

Table 3
Elemental compositions (expressed in ppm) determined by ICP-MS analysis of (a) Campi Flegrei, (b) Melos samples and (c) Melos samples after processing. <DL=below detection limit.

a

Sample no.	Location	Description	Li	B	Ti	V	Cr	Mn	Se	Rb	Sr	Y	Sb	Pb	Co	Ni	Cu	Zn	As	Cs	Ba
720.34	Pisciarelli	Area 1 on fumarole wall	<DL	<DL	83	15	<DL	<DL	<DL	9	72	<DL	<DL	14	<DL	<DL	4	<DL	<DL	<DL	280
720.35	Pisciarelli	Mudpool	<DL	6	98	12	<DL	2	<DL	7	72	<DL	<DL	19	0	<DL	<DL	<DL	<DL	<DL	258
720.36	Pisciarelli	Area 2 on fumarole wall	<DL	<DL	82	14	<DL	<DL	<DL	4	57	<DL	<DL	9	<DL	<DL	<DL	<DL	<DL	<DL	795
720.37	Pisciarelli	Blackish encrustation on fumarole wall	<DL	<DL	269	2	110	1	<DL	<DL	13	<DL	<DL	10	<DL	54	3	<DL	<DL	<DL	6567
720.38	Pisciarelli	Greenish encrustation on fumarole wall (same site L1 as in Piochi et al., 2015)	<DL	<DL	229	13	<DL	<DL	<DL	7	119	<DL	<DL	22	<DL	<DL	3	<DL	<DL	<DL	1890
720.40-	Solfatara	Area above the brick 'stuffe'/stoves	<DL	1	49	24	<DL	<DL	<DL	8	126	<DL	2	11	<DL	<DL	<DL	18	<DL	<DL	138
720.50	Pisciarelli	Mud pool (from Piochi et al., 2015, Table 2)	<DL	6	101	14	<DL	3	<DL	7	61	<DL	<DL	11	<DL	<DL	<DL	<DL	<DL	<DL	180
720.51	Pisciarelli	same sample Red 1_1/15 in Piochi et al. (2015)	<DL	<DL	307	90	<DL	<DL	<DL	2	97	<DL	<DL	36	<DL	<DL	<DL	<DL	74	<DL	405
720.52	Pisciarelli	Red alteration in site L1 of Piochi et al. (2015)	<DL	<DL	344	31	<DL	<DL	<DL	19	134	<DL	<DL	34	<DL	<DL	<DL	<DL	<DL	<DL	505
720.53	Pisciarelli	N wall to the mud pool	<DL	<DL	69	28	<DL	<DL	<DL	2	120	<DL	<DL	17	<DL	<DL	<DL	<DL	<DL	<DL	283
720.54	Solfatara	Cryptodome	<DL	5	62	9	<DL	<DL	<DL	<DL	141	<DL	<DL	22	<DL	<DL	<DL	65	<DL	<DL	412
720.55	Scarfoglio	Dense lithic at the Igloo, E Solfatara	<DL	<DL	113	6	<DL	<DL	<DL	2	34	<DL	<DL	8	<DL	<DL	<DL	<DL	<DL	<DL	54
720.55.1	Scarfoglio	White portion at the Igloo, E Solfatara	<DL	<DL	28	1	<DL	16	<DL	7	43	7	<DL	10	6	<DL	6	62	41	<DL	47
720.55.2	Scarfoglio	Reddish portion at the Igloo, E Solfatara	1	2	412	42	1	110	<DL	49	116	<DL	<DL	8	1	<DL	<DL	5	<DL	6	44

b

Sample no.	Location	Description	Li	B	Ti	V	Cr	Mn	Se	Rb	Sr	Y	Sb	Pb	Co	Ni	Cu	Zn	As	Ba
720.1	Fyriplaka cavern	Alum efflorescences	<DL	1	13	10	67	20	<DL	10	28	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	7
720.2	Loulos	White 'rock'	<DL	1	114	28	175	179	<DL	<DL	346	<DL	<DL	15	<DL	1	<DL	<DL	<DL	1346
720.3	Kalamos	White 'rock'	<DL	2	118	8	2	290	<DL	13	51	14	<DL	3	<DL	<DL	<DL	9	<DL	383
720.5	Kalamos	Alum efflorescences V	<DL	<1	6	6	<DL	163	<DL	21	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
720.6	Kalamos	Alum efflorescences IV	<DL	<1	4	5	20	76	<DL	12	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	20
720.7	Kalamos	Alum efflorescences VI with organic material	<DL	1	6	3	<DL	<DL	<DL	4	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	59
720.8	Kalamos	Alum efflorescences IV	<DL	<1	96	3	<DL	<DL	<DL	<DL	9	<DL	<DL	6	<DL	<DL	<DL	<DL	<DL	278
720.9	Kalamos	Alum efflorescences VII	<DL	<1	71	2	<DL	<DL	<DL	<DL	7	<DL	<DL	6	<DL	<DL	<DL	<DL	<DL	281
720.9	Kalamos	Alum efflorescences VII	<DL	<1	71	2	<DL	<DL	<DL	<DL	7	<DL	<DL	6	<DL	<DL	<DL	<DL	<DL	281
720.9.2 processed	Kalamos	Colloidal suspension of 720.9 after heating on hot plate	<DL	2	150	2	<DL	<DL	<DL	<DL	125	<DL	<DL	48	<DL	<DL	3	17	<DL	1245
720.9.3 processed	Kalamos	Solid undissolved fraction of 720.9 after drying in air	<DL	<1	96	1	<DL	<DL	<DL	<DL	18	<DL	<DL	9	<DL	<DL	<DL	<DL	<DL	394
720.13	Kalamos	Alum efflorescences VIII	<DL	<1	19	25	79	54	<DL	26	2	<DL	<DL	<DL	<DL	<DL	3	<DL	<DL	1
720.14b	Loulos	Alum efflorescences with white 'rock'	<DL	<1	49	<1	<1	<1	<DL	<DL	9	<DL	<DL	7	<DL	<DL	<DL	<DL	<DL	281
720.14b.1 processed	Kalamos	Soluble salts after evaporation	<DL	3	8	2	35	4	<DL	<DL	53	<DL	<DL	<DL	<DL	13	<DL	<DL	<DL	<DL
720.14b.3 processed	Kalamos	Undissolved solids	<DL	<1	37	1	<DL	<DL	<DL	<DL	8	<DL	<DL	6	<DL	<DL	0	<DL	<DL	255
720.18	Kalamos	Alum efflorescences IX	<DL	<1	24	10	53	16	<DL	7	13	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
720.18RT	Kalamos	Alum efflorescences IX	<DL	<1	21	9	46	13	<DL	6	10	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

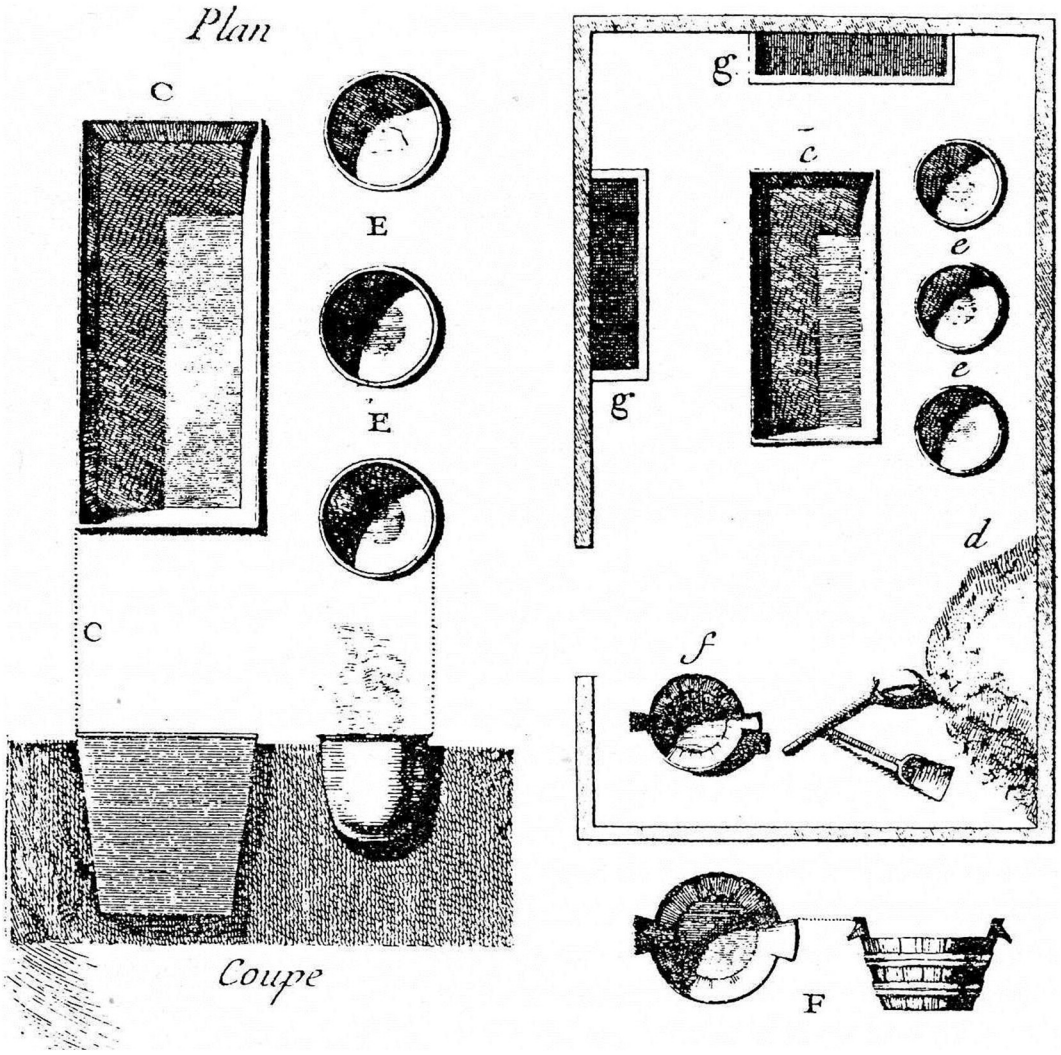

Fig. 5. Fougeroux's 1768 plan of a hut in Solfatara, Campi Flegrei where alum processing took place (reproduced from Singer 1948, Fig. 103).

tschermigite). For CF it could be Hg and As sulphides (cinnabar, realgar and orpiment) and for Melos, kaolinite and anatase. However, cinnabar has recently also been identified in Paleochori, Melos (Kati et al., 2015). The sampling strategy followed here was neither systematic nor exhaustive. Given that solfataric alum salts can vary depending on temperature and humidity, as well as the composition of the solfatara steam, the analyses of Table 2a–b should be viewed as indicative rather than exhaustive of minerals present, in either region.

There is documentary evidence for the simultaneous collection of cinnabar and ammonium salts at CF in the 18th century, as suggested by Hamilton (see documentary sources for Pozzuoli) but Hamilton's identification and, possible confusion, may have been based on colour similarity between cinnabar (HgS) and realgar (α-As_4S_4), both a striking red. Another difference between CF and Melos mineral assemblage is represented by the large amorphous component in CF. This may reflect preference in sampling (the 'fluffy' efflorescences of Melos were particularly targeted). However, it is the soluble aluminium sulphate salts that are of relevance to the present discussion, and so the absence of amorphous material has not been investigated further.

The second point concerns practices. The historical records associated with CF are particularly important in clarifying contemporary as well as earlier (Roman) practices. This means that solfataric alum in antiquity or later periods would have been processed in a manner not different from that described by Fougeroux and reproduced here in Fig. 5. The energy source would have been the sot soils of the solfatara, i.e. *c.* 100 °C. If, however, heating was well above that temperature range, it follows that minerals like millosceviscite or potentially also steklite could form. It is clear from Fourgeroux's plans that other minerals like ammonium chloride (salammoniac) or iron sulphate (green vitriol) were collected/enriched in separate containers from those associated with the alum

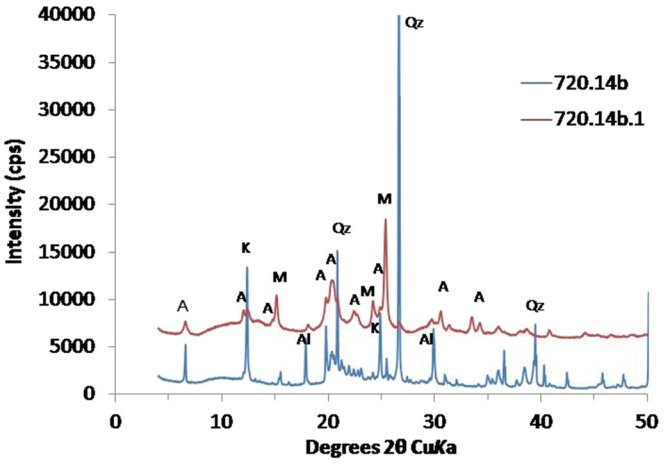

Fig. 6. XRD traces of samples 720.14b and 720.14b.1. Key to the symbols: A = alunogen, M = Millosevichite, Al = alunite, K = kaolinite, Qz = quartz.

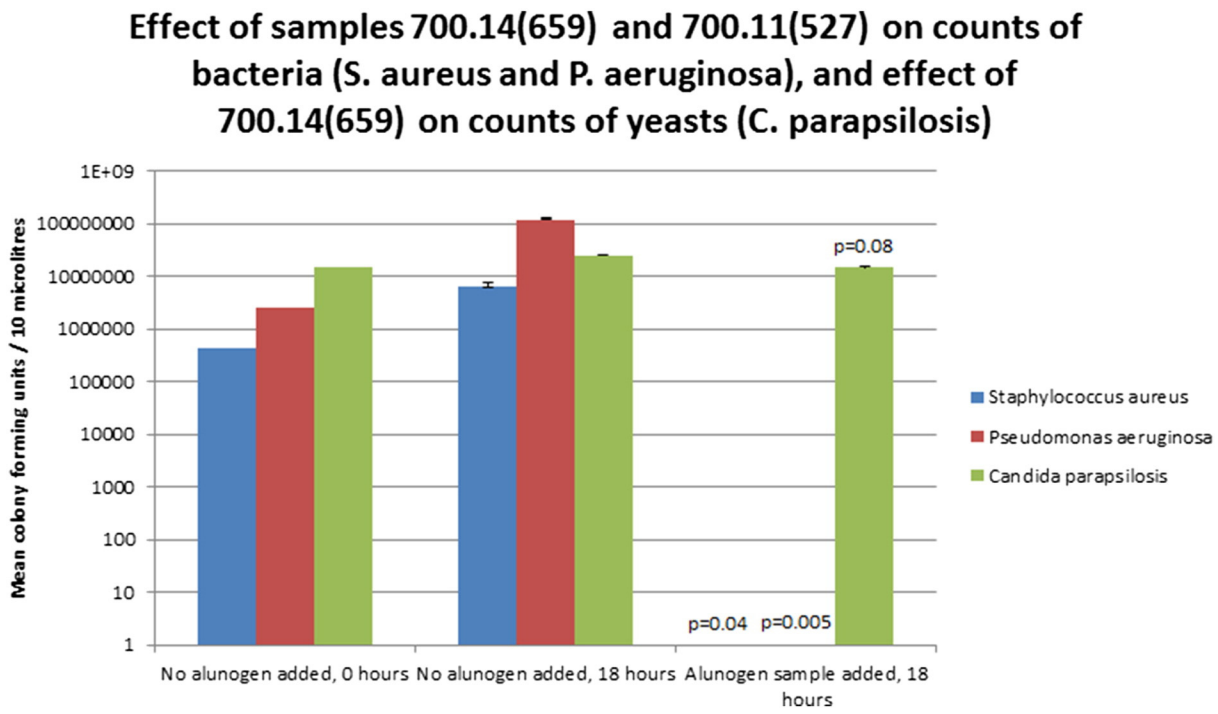

Fig. 7. Effect of alunogen samples on bacterial counts of *S. aureus* (blue), *P. aeruginosa* (red) and *C. parapsilosis* (green). Each bacterial strain (*S. aureus* and *P. aeruginosa*) was tested separately against two samples, 700.14(659) and 700.11(527). Sample 700.14(659) was also tested against the yeast *C. parapsilosis*. Addition of either sample caused bacterial counts to reduce to zero following overnight (18 h) incubation, demonstrating highly significant bactericidal effect. Conversely, addition of 700.14(659) has no statistically significant effect on microbial counts of *C. parapsilosis* (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

minerals, but the details of their extraction process seem to be less well documented.

The third point concerns the antibacterial properties of samples of solfataric alum. Basic microbiological testing of samples 700.14(659) and 700.11(527) demonstrated a considerable antibacterial activity against *Staphylococcus aureus* and *Pseudomonas aeruginosa*, which are gram positive and negative pathogens respectively. But there was no statistically significant effect on the yeast *Candida parapsilosis* when tested against sample 700.14(659). The two Kalamos samples are not mineralogically identical but they both contain alunogen and quartz and no elemental sulphur. The results suggest that their mineral combination has a mechanism of action which affects bacteria but not yeast. CF alunogen-rich samples are currently the subject of a separate microbiological investigation.

Pivotal to the action of alum minerals is the solubility of Al^{3+} within different mediums and at varying pHs. Aluminium does not possess an intrinsic biological function, and this is partly because life evolved near neutral pH where aluminium is insoluble. Al^{3+} is soluble at both high and low pHs. Soluble Al species are well known to be toxic to both eukaryotic and prokaryotic (bacterial) cells. Several possible mechanisms are discussed in the review by Pina and Cervantes (1996). In summary, aluminium inhibits the metabolism by substitution for magnesium in many metabolic reactions, such as ATP and DNA synthesis. Al^{3+} may also bind to the cell wall or ion pumps within the cell membrane, inhibiting ion transport.

The presence and role of sulphur (not included in ICP-MS analysis of Table 3) needs to be considered further. It is well established that CF and Melos samples (Table 2) contain significant quantities of elemental sulphur and other reduced sulphur species which are toxic to many bacteria. Sulphur may be both crystalline and amorphous. Sulphur is insoluble in water so it can be removed simply by filtration/centrifugation. The soluble components should be identified by ICP-MS, and tested separately for antibacterial activity to distinguish between surface and solution effects. Assuming that sulphur plays little part in the bactericidal action, it is important to confirm whether the Al^{3+} ions are solely responsible for the bactericidal effect. To that effect, Al^{3+} could be sequestered from solution by chelation to EDTA (ethylene diamine tetra-acetate), and the antimicrobial activity (MIC) of the EDTA and original solutions compared. The minimal inhibitory concentration (MIC) of alum-(K) has recently been reported (Bnyan et al., 2014).

The fourth point highlighted but not addressed here concerns the presence of microorganisms in the vicinity of alum minerals. Solfataras offer not simply a rich and varied mineral assemblage but also a world of microorganisms, the acidophiles or extremophiles known to inhabit geothermal environments (Gross, 2001; Ward et al., 2012). Relatively little is known about the nature of the microorganisms which appear to grow on the key aluminium sulphate minerals discussed here (Glamoclija et al., 2004; Pinto et al., 2007) although work has been carried out on the biota associated with acidic hot springs (Jones and Renaut, 2006). Microorganisms were observed around the entry to vents in both Melos (Fig. 4d) and Pisciarelli; they varied in colour from green to blue or black. They may include one or more diverse species, aerobic but also potentially anaerobic, living deep within the cavities. Presently we are undertaking microorganism identification work on samples from Melos, which may illuminate the nature of the relationship between solfataric alum minerals and microrganisms. It is possible that the latter may contribute to the antibacterial properties of the former.

To conclude, it may be worthwhile emphasising the significance of the study of Greco-Roman medicinal minerals beyond the confines of the Greco-Roman world. It appears that the medicinal minerals of Pliny and Dioscorides had their counterparts in other geographical regions. Browman and Gundersen's (1993) detailed study on the comestible/edible earths of the pre-Incas cultures of the Peruvian and Bolivian Highlands showed that they also consisted of layered silicates, sulphates and metal oxides. The authors reported that geophagic practices made use of illites, kaolinites and smectites as a means of absorbing/neutralising toxins. Furthermore, Browman and Gundersen (1993) suggest that alum efflorescences, also part of the pre-Incas *pharmacopoieia,* would almost certainly have been recovered from caves or sheltered

places. It is indeed from caverns and sheltered places, rather than open-air solfataras, that Melians in the Roman period removed the same efflorescences. These 'ancient' and difficult to date workings are revealed today as a result of modern open cast mining.

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